Validation of SAGE-III Measurements of NO_3: Ground-Based Vertical Profile Measurements

Status Report for the EOS Validation Program
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Goals of the Investigation

The SAGE III Science Team has established requirements for validation studies to assess the precision and accuracy of the SAGE III measurements of O_3, NO_2, H_2O, NO_3, $OClO$ and other trace species. The work described in this report is aimed at providing ground-based vertical profile and column measurements of NO_3 and NO_2 using the same methodology as the actual SAGE III technique, i.e. lunar and solar occultation in the UV/visible spectral region. Spectra are recorded using two different instruments: a 0.05 cm^{-1} interferometer (FTUVS) and a grating spectrograph which utilizes a diode array detector. Both instruments are located at the Table Mountain Facility of the Jet Propulsion Laboratory. Measurements are compared with results from the Caltech/JPL 1-d model to validate mechanisms of stratospheric NO_x chemistry.

Background

Interest in measurements of NO_3 stems from its role as a radical intermediate in the nighttime conversion of NO_x to NO_y. NO_3 is formed primarily in the reaction

$$NO_2 + O_3 \rightarrow NO_3 + O_2$$
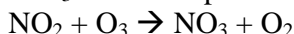
and removed by the reaction

$$NO_2 + NO_3 + M \rightarrow N_2O_5 + M.$$

The significance of this sequence lies in the fact that N_2O_5 is the anhydride of nitric acid, HNO_3, which is an important temporary reservoir of NO_x in the lower stratosphere. The conversion of N_2O_5 to HNO_3 in the stratosphere occurs on the surface of stratospheric sulfate aerosol (SSA) with high efficiency. The rate-limiting process in the conversion of NO_x to HNO_3 through these reactions is the $NO_2 + O_3$ reaction when the SSA surface area is elevated above background conditions. Under background conditions, or at altitudes that lie above the peak in the SSA vertical profile, the conversion rate is limited by the available aerosol surface area. Simultaneous measurements of NO_2, NO_3 and aerosol surface area are therefore key parameters in the understanding of the NO_x budget. Since NO_x plays an important role in the catalytic destruction of O_3 in the lower stratosphere, these measurements are crucial to the understanding of long-term trends in O_3.

Rapid photochemical destruction of NO_3 results in daytime mixing ratios that are extremely small. After sunset, however, this loss mechanism disappears causing NO_3 mixing ratios to increase rapidly. Lunar occultation is therefore an excellent method for the measurement of NO_3 using the technique of long-path visible absorption spectroscopy. While this technique has not yet been used from a satellite platform, it has been employed successfully from balloon

and ground-based sensors. The method takes advantage of the intense NO_3 (0,0) absorption band at 662 nm and another strong feature at 623 nm. The spectrum of NO_3 in this spectral region is well established from laboratory studies down to temperatures around 220 K. The spectroscopic determination of NO_3 is affected by interferences from the O_2 $b^1\Sigma_g^+(v=2) \leftarrow X^3\Sigma_g^-(v=0)$ band at 625 nm and a moderately strong water vapor band in the 640-665 nm spectral region. Despite its large cross sections at band peaks, the absorption features of NO_3 are quite weak with slant optical depths ranging from 0.01% to about 1% through the nighttime viewing period.

Methodology

With support from the EOS Validation Program, we have developed a measurement capability for NO_3 to provide correlative measurements for SAGE III and other future spaceborne UV-visible sensors including SCIAMACHY. The approach involves the use of a high resolution (0.05 cm^{-1}) Fourier Transform spectrometer (FTUVS) and a medium resolution grating spectrograph which incorporates a 1024-channel diode array detector. Both instruments operate in the UV-visible-NIR spectral region (0.29-1.1 μm). The FTUVS instrument is based on a plane-mirror Michelson design. The mirror drive is a parallelogram flexure mechanism driven by a voice coil actuator with a stroke of 5 cm. The fixed mirror is actively tilted to maintain alignment within 10% of an interference fringe at 300 nm over the entire stroke. The detector is a single-element silicon avalanche photodiode with a maximum gain of 300. Instrument control, data acquisition and spectral processing are accomplished using parallelized transputers. The grating spectrograph is a commercial 0.3 m Czerny-Turner instrument manufactured by Acton, Inc. The detector for the spectrograph is a commercial Reticon module cooled to –20 C. For applications involving relatively dim sources such as the Moon, the Reticon is superior to a charge-coupled device (CCD) detector due to its much larger well depth. The foreoptics for both instruments consists of a 32 in. dia. heliostat feeding an 8 in. off-axis telescope with f/3 optics. The telescope has dual collimating mirrors, one feeding the spectrometers and the other providing an image to a tracking camera for fine guidance of the heliostat. This capability permits the spectrometers to be pointed at specific features on the solar and lunar disks which is useful in a number of applications.

Accomplishments

Measurements of NO_3
Activities over the past year have been aimed at improving the measurement capability for NO_3 and developing a new capability for NO_2. Our initial efforts involved the use of the FTUVS interferometer operating at a resolution of 0.01 nm. The use of the high resolution instrument was motivated by the need to account properly for the spectral interference of water vapor. This problem is illustrated in Fig. 1. While the NO_3 spectrum is relatively broad and featureless, the water vapor spectrum in this region consists of a large number of resolved rotational lines. Since most of the water vapor in the column resides in the troposphere, these lines are significantly pressure broadened. The relative intensities are also affected by the vertical mixing ratio (vmr) profile of water which affects both the pressure broadening and the relative line intensities as a result of temperature variations. The spectrum is further affected by the instrument line shape function (ILS). The high spectral resolution of FTUVS should allow the

water vapor interference to be corrected with high precision provided that the spectral line parameters for water vapor are sufficiently accurate.

High resolution lunar spectra in the 655-670 nm region were recorded using FTUVS on several full moon viewing opportunities during 1998. While excellent spectra were obtained, we were not able to obtain NO_3 retrievals on a consistent basis. This was primarily due to the use of a bandpass filter that did not have sufficient rejection for residual radiation from the helium-neon reference laser used in FTUVS. In addition the passband characteristic of the filter was not properly centered on the NO_3 absorption feature. These factors resulted in small phase errors which affected the baseline stability of the spectra at the level of 0.1-1%. While small, these errors made it difficult to see the NO_3 feature was is normally very weak. To remedy this problem, a custom NO_3 bandpass filter with high rejection for the helium-neon laser line has been fabricated and will be tested on FTUVS in the near future.

As an alternative approach, we have set up a grating spectrograph/diode array detector instrument in addition to the interferometric spectrometer as described above. This instrument records absorption spectra over a 55 nm spectral interval centered at 662 nm. with a spectral resolution of 0.43 nm. With this instrument the time required to obtain a lunar spectrum under clear-sky conditions is typically 15 s. The minimum detectable absorbance is typically a few parts in 10^4. Four spectra are averaged for each acquisition The reference spectrum is a solar spectrum or a lunar spectrum after sunset before substantial NO_3 buildup has occurred. Wavelength calibration spectra are obtained periodically using a low-pressure neon lamp to correct for small wavelength offsets caused by temperature changes. Examples of lunar spectra are shown in Fig. 2.

Spectral processing to retrieve the NO_3 column density consists of the following steps:
0. subtraction of the detector fixed pattern noise from each spectrum,
0. wavelength calibration of the reference spectrum, shift and stretch of the wavelength scale for each lunar spectrum to minimize the residual solar and water vapor lines when compared with the reference spectrum,
0. computation of the atmospheric absorption spectrum
0. simultaneous fitting of the water vapor and NO_3 features along with a second-order polynomial to account for absorption due to Mie scattering, Rayleigh scattering, temperature-dependent baseline changes. The conjugate gradient method is used as the fitting algorithm. The NO_3 reference spectra are taken from the work of Sander (1986). The water vapor reference spectra are calculated as described below. An example of a lunar absorbance spectrum is shown in Fig. 3 along with reference spectra for NO_3 and water vapor. Absorption bands due to both NO_3 and H_2O are clearly seen in this example.

An important aspect of the NO_3 retrieval is the proper correction for the water vapor interference. This is complicated by the highly variable nature of the tropospheric water vapor distribution and the sensitivity of the spectral band shape to this distribution. In our forward model, two line-by-line spectral simulation codes (LBLRTM, Clough et al., and an in-house code, Nemtchinov et al.) were intercompared using the HITRAN line parameters for water vapor in the 640-665 nm spectral region. The model used a water vapor profile based on balloon sonde hygrometer soundings. While the forward model captures most of the observed spectral features, the residuals in the water vapor band are still fairly large. We have concluded that the residuals are due primarily to errors in the assumed water vapor vmr profile, and with possible errors in the HITRAN line parameters. We are investigating the use of a retrieval code which will optimize the water vapor fits with the use of a model atmosphere with 3-5 vertical levels (2-4

levels in the troposphere, 1 in the stratosphere). In addition, laboratory investigations are underway elsewhere to improve the accuracy of the water vapor line list.

Lunar measurements using the grating spectrometer began in November, 1998 and have continued through each subsequent full moon opportunity. The diurnal variation of the NO_3 column density at Table Mountain Facility on the dates of March 2, 1999 and April 28, 1999 are shown in Figure 4. These results show that NO_3 can be successfully measured with excellent temporal resolution starting immediately after sunset when NO_3 levels are near their minimum values. Large variability in the observed measurements has been observed. Some of this variability is due to tropospheric NO_3 which is influenced by the NO_x sources within the Los Angeles area. The precision and accuracy of these retrievals are currently being assessed.

Measurements of NO_2

While the formal scope of our SAGE III Validation project is limited to measurements of NO_3, we have discovered recently that we can easily make daytime measurements of NO_2 column densities. Since NO_2 is one of the key scientific objectives of the new SAGE III instrument, these measurements will hopefully complement our existing validation efforts.

The NO_2 measurements are carried out using the FTUVS interferometer operating at a spectral resolution of 0.05 cm^{-1} (0.0009 nm). At this resolution, NO_2 vibronic features can be seen clearly at wavelengths near 425 nm. The atmospheric spectrum is broadened compared with laboratory reference spectra obtained at the same resolution most likely because of pressure broadening. This suggests that the NO_2 vertical profile can be retrieved, perhaps with a resolution of 1-2 scale heights. Because there are a few segments of the NO_2 spectrum that occur where there are no measurable solar lines, the NO_2 measurements can be performed without the need to ratio against a reference spectrum. The NO_2 features can be observed clearly at solar zenith angles which exceed about 60 deg. Reference spectra for NO_2 covering the relevant atmospheric pressure and temperature ranges are not currently available at this resolution. This represents an important need area in order to interpret these measurements fully.

Planned Activities

The activities for the coming year may be summarized as follows:

NO_3 Measurements

1. Improvements to the instrument are planned including active temperature control of the spectrograph housing to minimize wavelength calibration errors and replacement of the diode array detector with a new model. With supplementary support from the EOS Validation Program that has been recently received, the spectrograph will be moved to a new laboratory at TMF (TM-28) specially constructed for remote sensing applications such as this one. The spectrograph will have a dedicated heliostat so that both the spectrograph and the FTUVS interferometer can be operated independently.
1. NO_3 measurements will be made using the FTUVS instrument with a new 662 nm interference filter that should significantly improve the baseline stability of the instrument. These measurements will be made at 0.05 nm spectral resolution which should simplify the analysis of spectral interference by water vapor.
1. Studies will be carried out to determine if a multi-layer water vapor vmr profile can be retrieved, and to determine if this will improve the accuracy of the NO_3 retrievals.
1. NO_3 measurements will be carried out at every full moon viewing opportunity, weather permitting.

NO$_2$ Measurements

1. Work will continue on an algorithm for NO$_2$ retrievals using FTUVS spectra taken at 0.05 cm^{-1} resolution. This will include an analysis of the feasibility of coarse vertical profile retrievals from daytime solar absorption spectra.
1. Efforts will be made to obtain NO$_2$ reference spectra over a range of pressure and temperature relevant to the atmosphere.
1. Following the launch of SAGE III, NO$_2$ observations will be coordinated with spacecraft overpasses as often as possible. Discussions with SAGE III investigators will determine the frequency and timing of the observations.

Modeling

1. The JPL/Caltech 1-d atmospheric model will be used in the analysis of NO$_2$ and NO$_3$ measurements from FTUVS and the spectrograph. Comparisons will be made between measurements and model calculations of the NO$_3$ column constrained by measurements of NO$_2$ from the spectrograph, the O$_3$ vmr from the DIAL system at TMF, NCEP temperature profiles and other relevant trace species measurements from UARS and other spacecraft. The results will be used to assess the adequacy of existing models of stratospheric NO$_x$ chemistry.

<u>Schedule</u>

Tasks are referenced to the numerical levels in the previous paragraphs

Task/ Month	July	Aug	Sept	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun
NO$_3$												
1												
2												
3												
4												
NO$_2$												
1												
2												
3												
Models												
1												

Collaboration with the SAGE III Instrument Team:

There are several areas of mutual interest between our group and the SAGE III Instrument Team including:

- comparison of retrieval algorithms for NO_3 and other species using lunar spectra
- treatment of interfering spectral features
- use of a common spectroscopic database for NO_3 and other molecules
- methods for the comparison of SAGE III vertical profiles with the column and profile data obtained from ground-based sensors
- separation of the NO_3 contributions from the stratosphere and troposphere, especially where regional NO_x sources are important

The PI of this task attended the SAGE III Science Team meeting in Tucson in February, 1999 and presented a talk outlining the objectives and progress of the NO_3 measurements. Attendance at the next Science Team meeting in October is anticipated.

Exchange of Correlative Data with Instrument Team and Other Investigators: It is our intention to disseminate the correlative data from this investigation to the Instrument Team as quickly as possible. While a protocol for this exchange has not yet been established, this will be accomplished well in advance of the SAGE III launch. Data from the correlative measurements will be available on our ftp site for rapid dissemination to interested users.
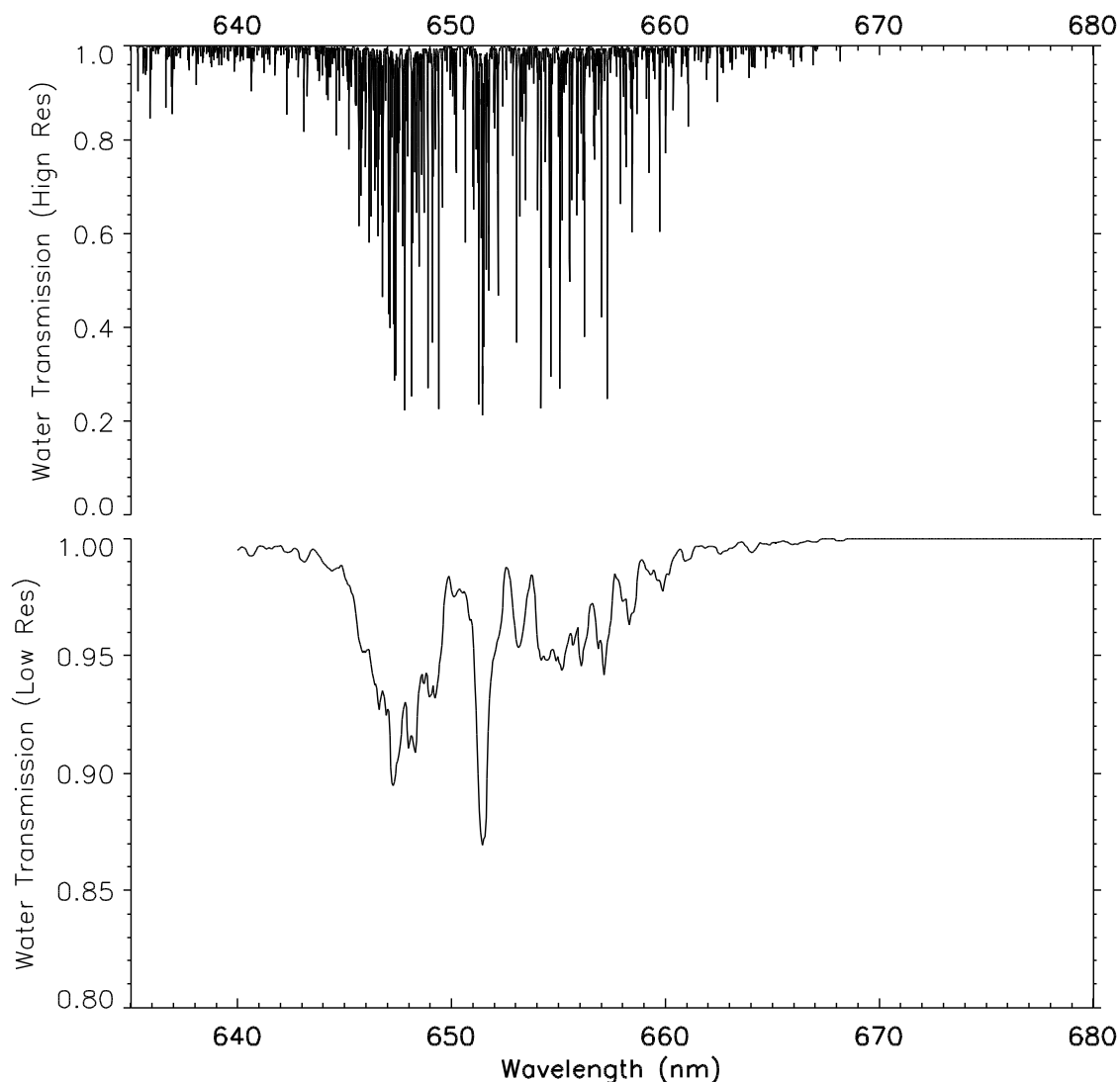
Figure 1. Absorption spectrum of water vapor in the 635-670 nm spectral range from HITRAN (upper panel). Simulated atmospheric water vapor spectrum computed using a line-by-line code (LBLRTM, Clough *et al.*) convolved with the instrument lineshape function of the grating spectrograph. Since many of the water lines are saturated at high zenith angles, the low resolution spectrum shows a highly nonlinear curve of growth.
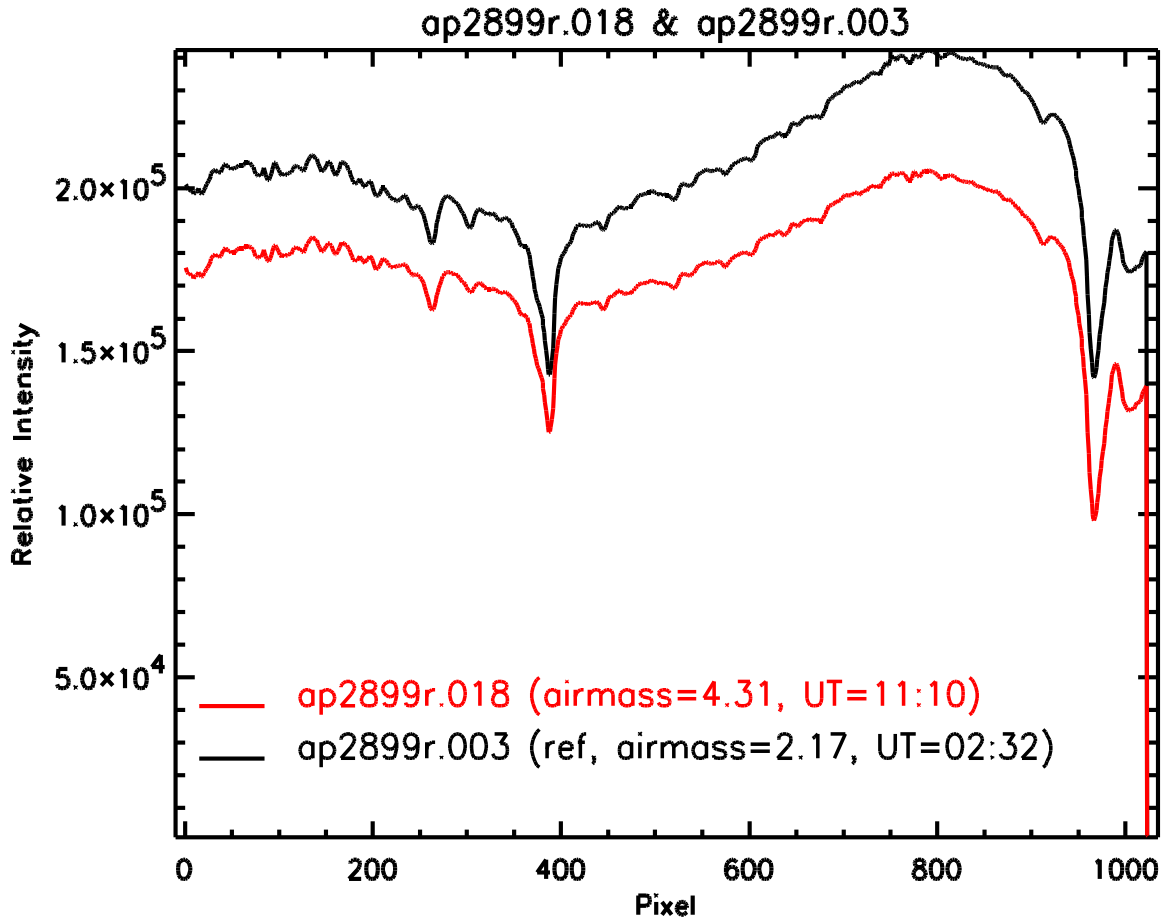
Figure 2. Examples of lunar spectra from April 28, 1999 before wavelength calibration. The prominent absorption feature near pixel 400 is the solar Balmer- line while the feature near pixel 950 is due to atmospheric O_2.
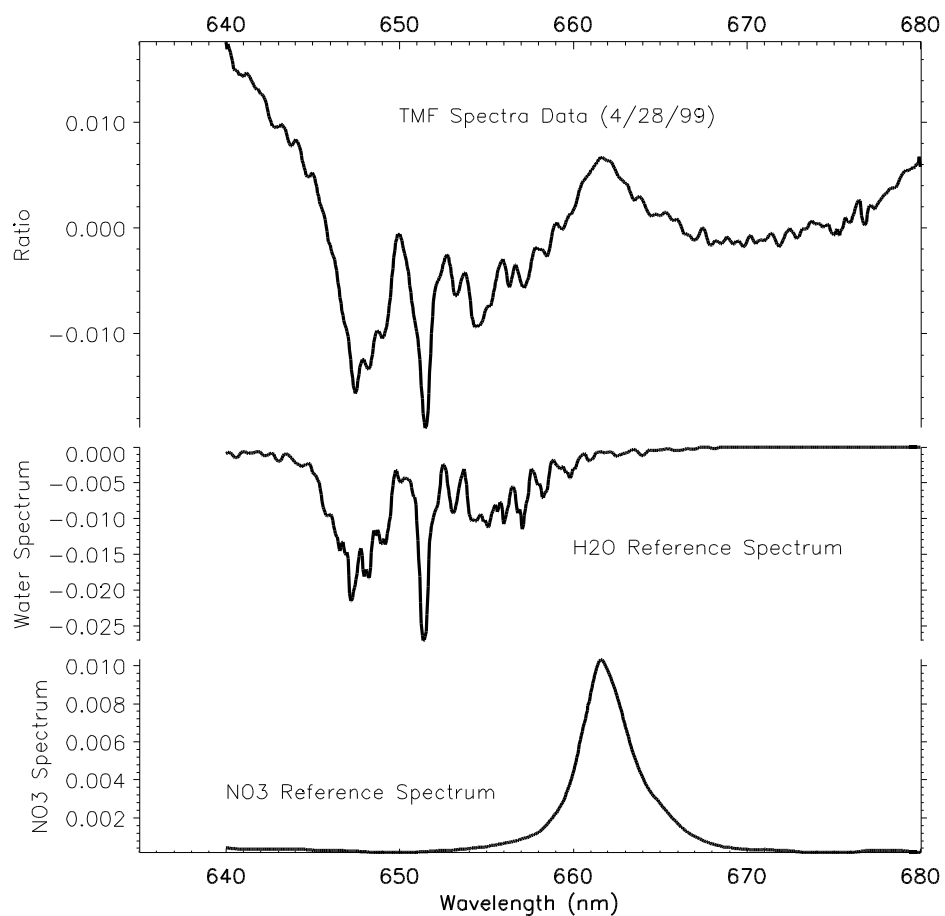
Figure 3. Absorbance spectrum derived from the ratio of moonset/moonrise spectra. Data were acquired using the grating spectrograph on April 28, 1999. Water vapor and NO_3 are clearly visible (upper panel). Simulated water vapor reference spectrum (middle panel). NO_3 reference spectrum (lower panel).
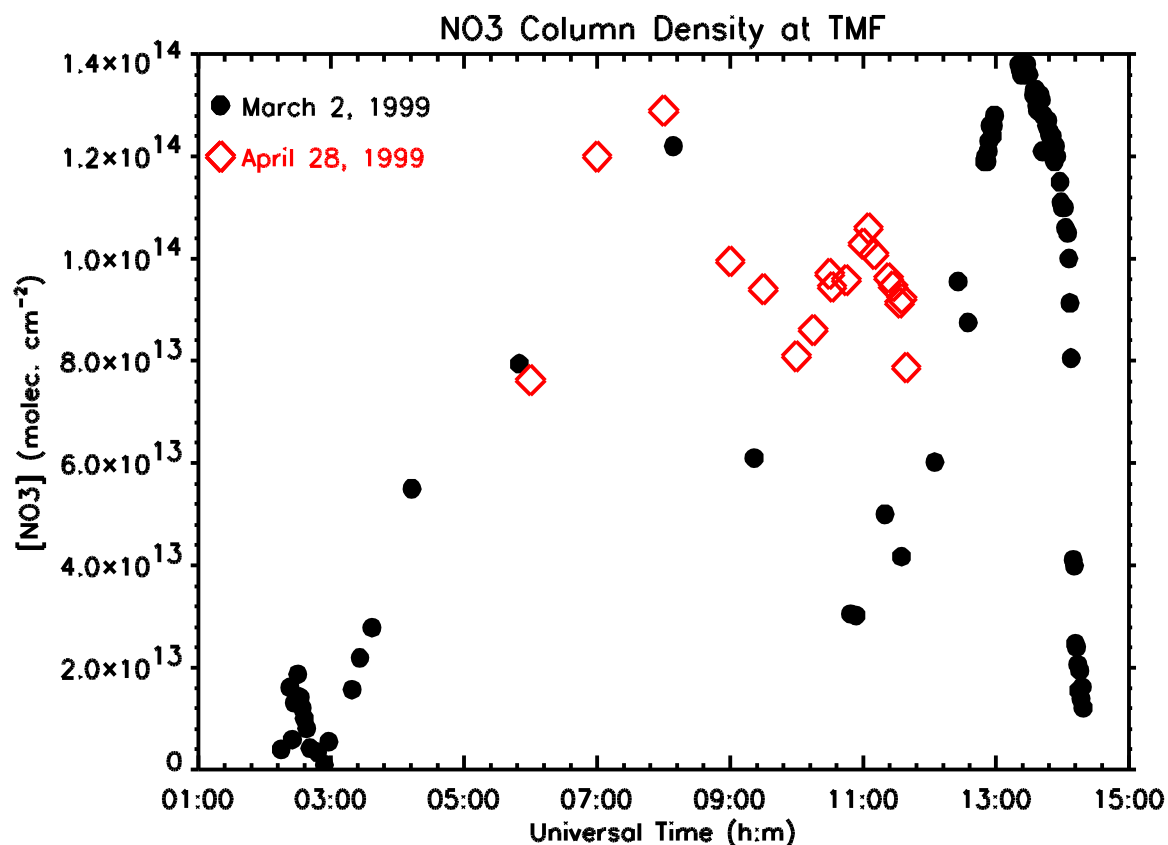
Figure 4. Variation of nighttime column NO$_3$ density at TMF on March 2, 1999 (black dots) and April 28, 1999 (red diamonds). The detection limit is 0.5×10^{13} molec. cm^{-2}. The large variations in the column through the diurnal cycle are indicative of local tropospheric NO$_x$ sources.